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(71) Applicant: Sumitomo Chemical Industries Ltd.  
15, Kitahama 5 chome  
Higashi-ku, Osaka-shi(JP)

(72) Inventor: Funaki, Yuji  
10-3-356, Sonehigashinocho-2-chome  
Toyonaka-shi(JP)

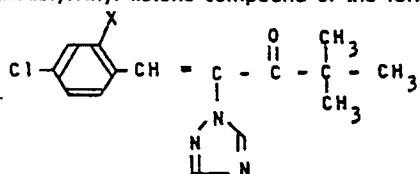
(72) Inventor: Tanaka, Shizuya  
2-11, Niina-4-chome  
Minoo-shi(JP)

(72) Inventor: Matsuo, Noritada  
29-2, Terayamamichi Minamino  
Itami-shi(JP)

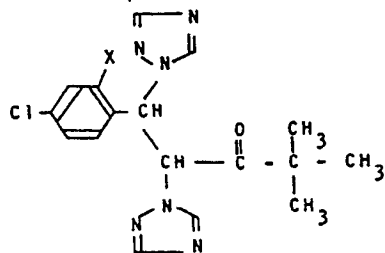
(74) Representative: Overin, Alison Diana et al,  
J.A. KEMP & CO. 14, South Square Gray's Inn  
London WC1R 5EU(GB)

(54) Production of triazolyvinyl ketones.

(57) A triazolyvinyl ketone compound of the formula:



wherein X is a hydrogen or chlorine atom, is produced by heating a novel compound of the formula:



wherein X is as defined above.

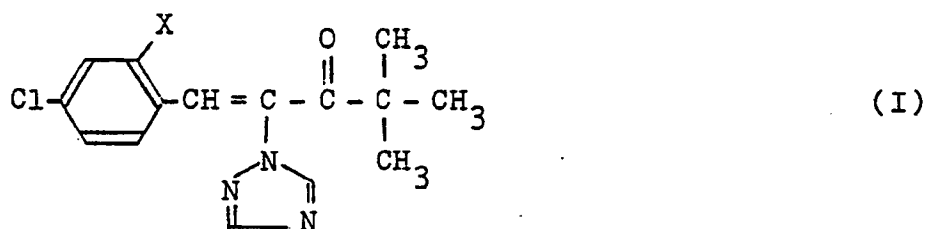
The triazolyvinyl ketone compound is useful as an agricultural fungicide.

EP 0 046 658 A2

## PRODUCTION OF TRIAZOLYLVINYL KETONES

1           The present invention relates to a process for producing an antimicrobial triazolylnyl ketone derivative.

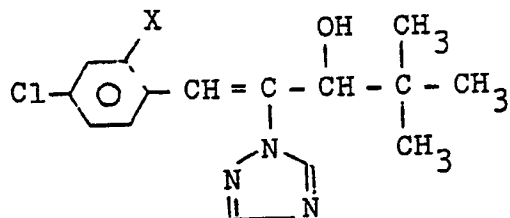
          More particularly, it pertains to an improved  
5 process for the production of a fungicidal triazolylnyl ketone compound of the formula:



wherein X is a hydrogen or chlorine atom, and to an intermediate compound used therein.

          It has been known that the said triazolylnyl  
10 ketone compounds of the formula (I) are useful as agricultural fungicides [Japanese Patent Publication (unexamined) No. 130661/1978].

          It has also been known that these compounds are useful as the intermediates for the production of  
15 fungicidal triazolylnyl alcohol compounds of the formula:



- 1 wherein X is as defined above [U.S. Patent  
4,203,995; Japanese Patent Publication (unexamined)  
No. 41875/1979].

5 In view of the excellent fungicidal property  
of these compounds, we have intensively studied on the  
commercial production of these compounds, and found that  
the said triazolylvinyl ketone compounds can readily  
and advantageously be prepared in a high yield by the  
following method:

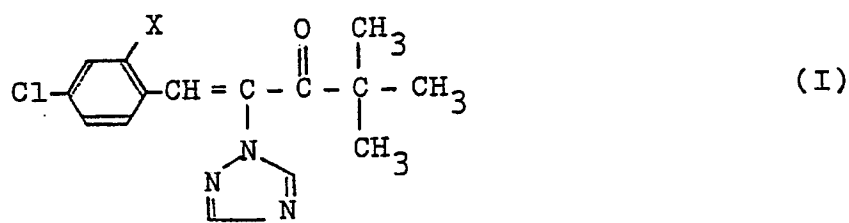


1 wherein X means a hydrogen or chlorine atom, and Y  
means a hydrogen or chlorine atom or a methyl group.

In the synthetic method of the present invention,  
the triazolylvinyl ketone compounds (I) can be obtained  
5 from benzalpinacolone compounds (VII) by the 4, 5 or 6  
step-operation as shown in the above scheme, and each  
of these steps affords good yield.

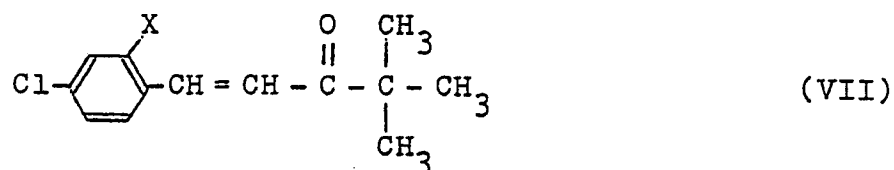
The starting material, benzalpinacolones (VII)  
can readily be prepared by the condensation of benzalde-  
10 hyde derivatives and pinacolone in an almost quantitative  
yield in a conventional manner. Other advantageous aspect  
of the process of the present invention is that phenyl-  
sulfinic acids and triazole can be recovered and recycled  
to minimize the consumption of these reagents in the  
15 process.

Thus, the present invention provides a process  
for producing a compound of the formula:



wherein X is a hydrogen or chlorine atom, which process  
comprises the steps of:

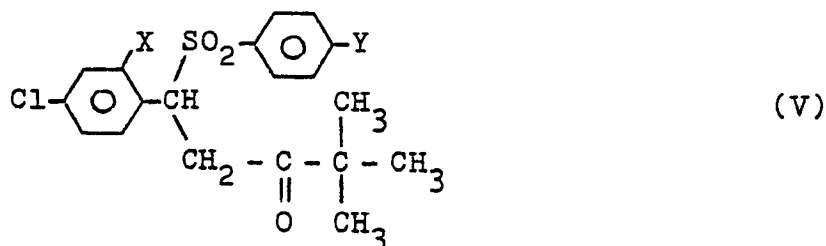
20 (a) reacting a benzalpinacolone derivative of the  
formula:



- 1 wherein X is a hydrogen or chlorine atom, with a compound of the formula:



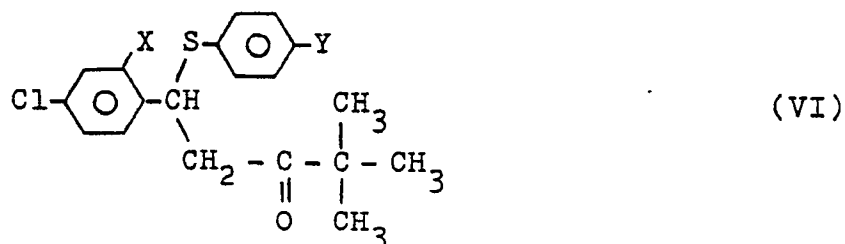
- wherein Y is a hydrogen or chlorine atom, or a methyl group, to give a compound of the formula:



- 5 wherein X is as defined above, or with a compound of the formula:

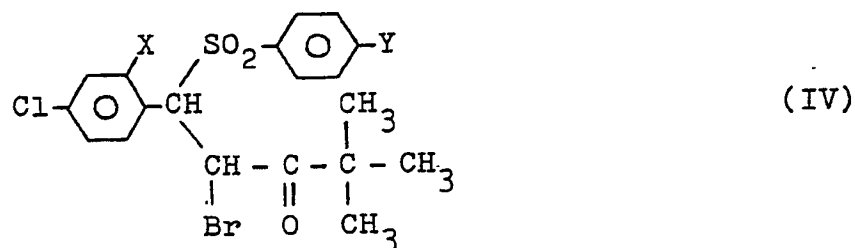


- wherein Y is as defined above, to give the compound of the formula:



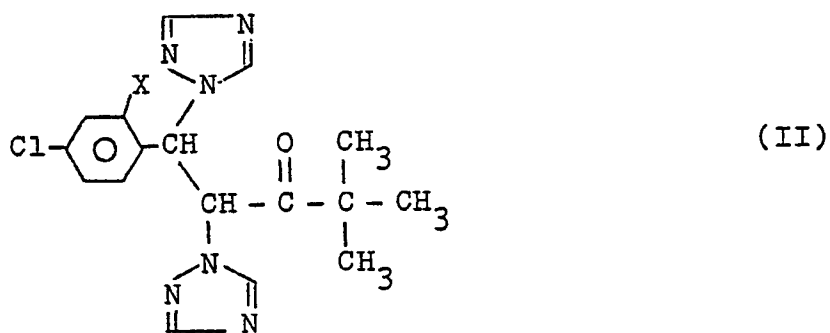
1 wherein X and Y are as defined above, which is then  
reacted with an oxidizing agent to give the compound  
of the formula (V);

(b) reacting the compound of the formula (V) with  
5 a brominating agent to give a compound of the formula:

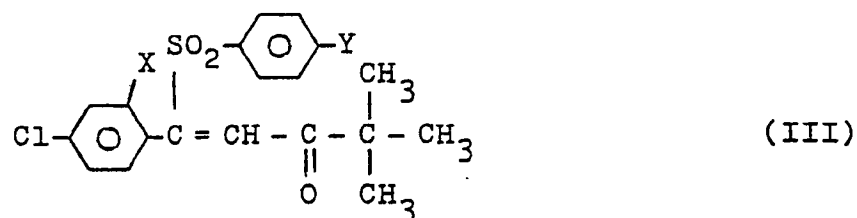


wherein X and Y are as defined above;

(c) reacting the compound of the formula (IV) with  
triazole in the presence of a base to give a compound  
of the formula:



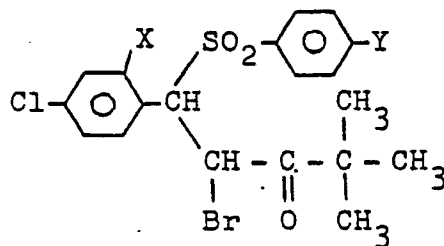
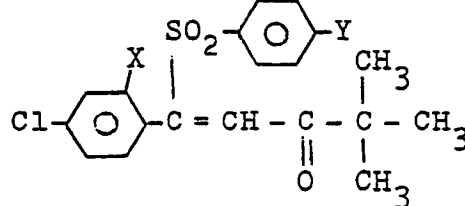
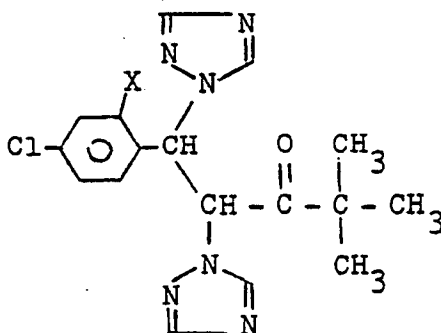
10 wherein X is as defined above, or with a base to  
give a compound of the formula:



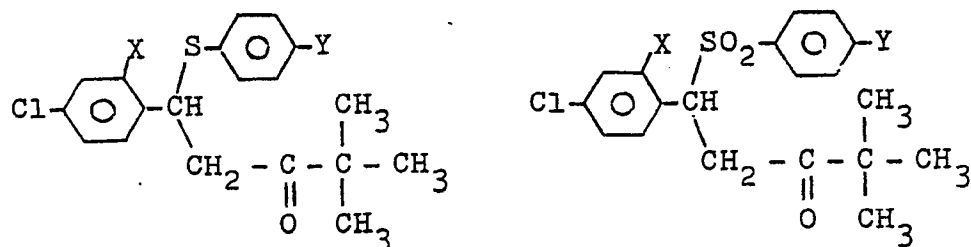
1 wherein X and Y are as defined above, which is then reacted with triazole to give the compound of the formula (II); and

(d) heating the compound of the formula (II) to give said compounds (I).

It also provides useful intermediate compounds having the following formulae:



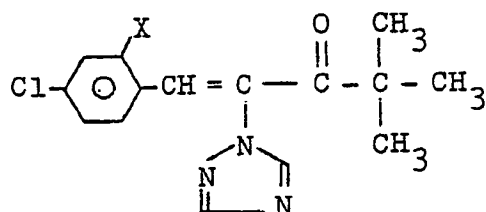




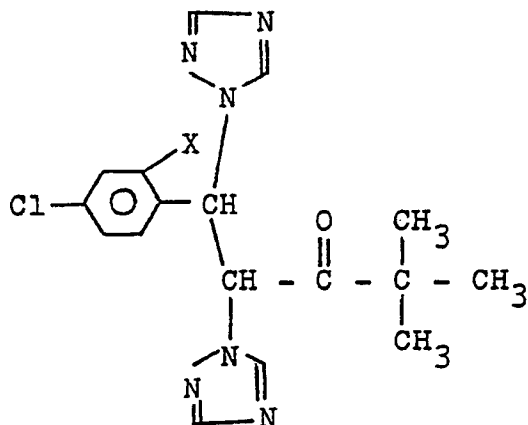
1 wherein X and Y are as defined above, and processes  
for producing the same.

The compounds of the present invention are  
isomeric, and it is to be understood that the present  
5 invention is contemplated to include optical and  
geometrical isomers thereof.

In the present invention, the compounds of  
the formula (I):



wherein X is as defined above, is prepared by heating  
10 the compounds of the formula (II):



- 1 wherein X is as defined above, thereby decomposing  
the compounds to give the desired compounds (I).  
This heat-decomposition process can be carried out  
either in a suitable solvent or without any  
5 solvent.

Examples of suitable solvents are ketone-  
solvents such as acetone or methyl ethyl ketone,  
halogenated hydrocarbons such as carbon tetrachloride,  
chloroform, or dichloroethane, aromatic hydrocarbons  
10 such as benzene, toluene, xylene, chlorobenzene,  
dichlorobenzene or trichlorobenzene, nitriles such  
as acetonitrile or propionitrile, ethers such as  
dioxane, tetrahydrofuran or diethylene glycol  
dimethyl ether, dimethylformamide, dimethylsulfoxide,  
15 hexamethylphosphoramide and water. The temperature  
at which the heating of the compound (II) is effected

1 is in a range of from 50°C to 200°C, preferably 80°C to 200°C.

5 The products (I) may be isolated from the reaction mixture by extracting with water-immiscible solvents after diluting the reaction mixture with water. And, from the remaining aqueous layer, triazole may be recovered with high recovery rates by extracting under basic and basic conditions, respectively.

10 The bistriazolyl ketone compounds (II) can be prepared from the compounds of the formula (IV) by the following two methods:

The first method is the conversion of the compounds of the formula (IV) to the compounds (II) with  
15 triazole. This process is carried out by reacting the compounds (IV) with triazole in the presence of a base in a suitable solvent. Examples of the bases used in this process are carbonates such as potassium or sodium carbonates, acetates such as potassium or sodium  
20 acetates, hydroxides of metals such as potassium, sodium or calcium hydroxides, and tertiary amines such as triethyl amine or pyridine. Among these bases, carbonates are preferable.

Examples of the solvents are ketones such  
25 as acetone or methyl ethyl ketone, nitriles such as acetonitrile or propionitrile, aromatic hydrocarbons such as benzene, toluene or xylene, ethers such as tetrahydrofuran, dioxane or diethyl ether, dimethyl

1 formamide, dimethylsulfoxide and hexamethylphosphoramide.  
In this process, water, alone or in combination with  
the said organic solvents, may also be used as a solvent.  
The reaction temperature may be from 0°C to the boiling  
5 point of the used solvent, preferably from 50°C to the  
boiling point of the used solvent.

Triazole is used in an amount of 2 - 5 moles,  
preferably 2 - 3 moles per 1 mole of the compounds (IV).  
The amount of the bases used in this process is 2 moles  
10 or more per 1 mole of the compounds (IV). The product  
is readily isolated in a conventional manner after removing  
the salts of the used base and hydrobromic acid and the  
phenylsulfinic acid compounds (VIII) by filtration or  
dissolving in water.

15 Alternatively, the compounds (II) can also  
be prepared by converting the compounds (IV) to the  
compounds (III) with a base, and then reacting the  
compounds (III) with triazole. More specifically, the  
first step can be carried out by reacting the compounds  
20 (IV) with at least equimolar amounts of a base.  
Examples of the bases are carbonates such as potassium  
or sodium carbonates, acetates such as potassium  
or sodium acetates, metal hydroxides such as potassium,  
sodium or calcium hydroxides and tertiary amines such  
25 as triethyl amine or pyridine, and carbonates and metal  
hydroxides are preferable. Triazole may also be used  
as a base in this process.

In general, it is advantageous to effect the

1 reaction in a solvent except the case where a tertiary  
amine is used therein. Examples of suitable solvents  
are ketones such as acetones or methyl ethyl ketone,  
nitriles such as acetonitrile or propionitrile, aromatic  
5 hydrocarbons such as benzene, toluene or xylene, ethers  
such as diethyl ether, dioxane or tetrahydrofuran,  
dimethylformamide, dimethylsulfoxide, and hexamethyl-  
phosphoramide. The reaction may also be carried out  
in water, alone or in homogeneous or multiphase combina-  
10 tion with the said solvents. The reaction temperature  
is usually in a range from 0°C to the boiling point of  
the used solvent, but, when a strong base such as metal  
hydroxide is used, the reaction smoothly proceeds at  
such a low temperature as 0°C or so. The amounts of the  
15 bases is usually 1 to 5 moles, preferably 1 to 3 moles  
per 1 mole of the compounds (IV). The isolation of the  
compounds (III) can readily be carried out in a con-  
ventional way, for example, by extracting with a water-  
insoluble solvent followed by evaporation. When the  
20 reaction is carried out in a water-soluble solvent, the  
reaction mixture is diluted with water, and the products  
are crystallized and isolated by filtration.

The second step, the conversion of thus obtained  
compounds (III) to the compounds (II) is accomplished  
25 by reacting the compounds (III) with triazole. This  
process can advantageously be effected in the presence  
of a base in amounts of 2 moles or more, preferably 2.05  
to 5 moles per 1 mole of the compounds (III). This

1 synthetic method can continuously be carried out without  
isolation of the compounds (III). Thus prepared com-  
pounds (II) can readily be isolated in a conventional  
manner as mentioned previously.

5           The compounds (IV) can be obtained by reacting  
the compounds (V) with a brominating agent. As a brominat-  
ing agent of this reaction, bromine, N-bromosuccinimide  
and other brominating agents which are usually used for  
the bromination of ketone compounds can be used. These  
10 brominating agents are used in an amount of 1 mole or  
more, preferably 1 to 2 moles per 1 mole of the compounds  
(V). It is preferable to carry out the reaction in the  
presence of a solvent. Halogenated hydrocarbon such as  
carbon tetrachloride, chloroform or dichloroethane,  
15 halogenated aromatic hydrocarbon such as chlorobenzene  
or dichlorobenzene, ether such as diethyl ether, dioxane  
or tetrahydrofuran, water, methanol, pyridine, dimethyl-  
formamide and acetic acid can be used as a solvent. The  
reaction is usually carried out at a temperature of  
20 from 0°C to the boiling point of the used solvent. The  
products may readily be isolated by a method conven-  
tionally used in the bromination process. For example,  
the reaction mixture is diluted with water, and extracted  
with a solvent insoluble in water or filtrating the  
25 precipitated products.

The compounds (V) may be prepared by reacting  
the compounds (VII) with one to 3 equimolar amounts of  
the compounds (VIII) in a suitable solvent at a temperature

1 of from 0°C to the boiling point of the used solvent.  
Generally speaking, the compounds (V) is prepared in  
a quantitative yield by this reaction. Examples of  
solvents suitable to this process are alcohols such as  
5 methanol, ethanol or propanol, hydrocarbons such as  
benzene, toluene or xylene, ketones such as acetone  
or methyl ethyl ketone, nitriles such as acetonitrile or  
propionitrile, ethers such as diethyl ether, tetrahydro-  
furan or dioxane, dimethylformamide, dimethylsulfoxide  
10 and the like. Mixed solvents of these organic solvents  
and water may also be used. When the reaction is  
conducted in the presence of a base such as pyridine or  
Triton B or sodium phosphite in amounts of 0.01 to 2.0  
moles per 1 mole of the compounds (VII) a good result  
15 is obtained.

The compounds (V) may also be prepared by  
the oxidation of the (VI) with a suitable oxidizing  
agent. Examples of the oxidizing agents are hydrogen  
peroxide, organic acid peroxides, potassium permanganate,  
20 sodium metaperiodate, nitric acid, sodium hypochlorite,  
ozone, chromic acid and the like, and preferred are  
hydrogen peroxide, organic acid peroxides and ozone.  
In general, it is preferable to carry out the reaction  
in the presence of a solvent. Organic solvents which  
25 are inert to the used oxidizing agent, whether alone or  
in combination with the other inert solvents, can be  
used, and particularly preferred are halogenated  
hydrocarbons such as carbon tetrachloride, dichloro

- 15 -

1 methane or chloroform, ketones such as acetone or methyl  
ethyl ketone, acetic acid and water. The reaction is  
usually carried out at a temperature of from  $-50^{\circ}\text{C}$  to  
100 $^{\circ}\text{C}$ , preferably  $-10^{\circ}\text{C}$  to  $80^{\circ}\text{C}$ . With respect to the  
5 amounts of the oxidizing agents, the oxidation of 1  
mole of the compounds (VI) requires 2 moles of active  
oxygen. For example, in case of hydrogen peroxide, 2  
moles is required for the oxidation of 1 mole of the  
compounds (VI). It is, however, desirable to use the  
10 oxidizing agent in small excess to eliminate bad odor  
caused by the thiophenol derivatives remaining in  
the compounds (VI). The isolation of the products can  
readily be carried out by diluting the reaction mixture  
with water, and extracting with a water-immiscible solvent,  
15 or crystallizing the products and collecting them by  
filtration. The compounds (VI) can be prepared in a  
good yield by the reaction of the compounds (VII) with  
the compounds (IX). The reaction can be carried out in  
an organic solvent such as alcohols (e.g., methanol,  
20 ethanol, propanol, etc.), aromatic hydrocarbon (e.g.,  
benzene, toluene, xylene, etc.), ketones (acetone, methyl  
ethyl ketone, etc.), nitriles (e.g., acetonitrile,  
propionitrile, etc.), ethers (e.g., diethyl ether,  
tetrahydrofuran, dioxane, etc.), dimethylformamide, or  
25 dimethylsulfoxide. As a solvent, aqueous mixture of  
these solvents may also be used. The reaction can be  
carried out at a temperature of from  $0^{\circ}\text{C}$  to the boiling  
point of the used solvent. Generally, 1 mole of



1 the compounds (VII) is reacted with 1 to 3 moles of the  
compounds (IX), preferably in the presence of a basic  
catalyst in amounts of 0.001 to 1 mole per 1 mole of the  
compounds (VII). Examples of the basic catalysts are  
5 sodium hydroxide, potassium hydroxide, sodium carbonate,  
potassium carbonate, sodium bicarbonate, triethylamine,  
dimethylaniline, pyridine, and Triton-B. The compounds  
(IX) may be used in the form of potassium or sodium  
salts for this process.

10           The compounds (VII) can readily be prepared  
by a conventional method as previously mentioned (Organic  
Synthesis, Col. Vol. I, p.81, and C.A., 84: p 73606u;  
63: 1726f). The following examples are given to illust-  
rate the present invention more precisely, but it is  
15 not intended to limit the present invention thereto.

#### Example 1

##### Synthesis of 1-(4-chlorophenyl)-4,4-dimethyl-1-phenylthiopentan-3-one:-

To a mixture of 4-chlorobenzalpinacolone  
20 (22.3 g), triethylamine (5 drops) and ethanol (250 ml)  
was added thiophenol (12 g) and the mixture was kept to  
70°C for 4 hours. After ice-cooling, the resulted  
precipitates were collected by filtration, washed with  
cold ethanol and dried to give white crystals of  
25 the captioned compound (29 g; 84%). m.p. 127 - 128°C.

- 17 -

1	Elementary analysis	C(%)	H(%)	S(%)	Cl(%)
	Found	68.55	6.33	9.72	10.45
	Calculated (as $C_{19}H_{21}OSCl$ )	68.54	6.37	9.63	10.65

## Example 2

5     Synthesis of 1-(4-chlorophenyl)-4,4-dimethyl-1-phenylsulfonylpentan-3-one:-

1-(4-Chlorophenyl)-4,4-dimethyl-1-phenylthiopentan-3-one (18 g) was dissolved in chloroform (500 ml). m-Chloroperoxybenzoic acid (24 g) was gradually  
 10 added to the mixture in 1 hour. The mixture was then stirred at 20°C for 3 hours. The mixture was washed with 5% sodium hydrogen sulfite aqueous solution and sodium bicarbonate aqueous solution, and concentrated. The solid residue was then treated with ethanol to give  
 15 crystals, which were collected by filtration and dried to give 18.8 g of the captioned compound.  
 m.p. 145 - 146°C.

	Elementary analysis	C(%)	H(%)	S(%)	Cl(%)
	Found	62.71	5.73	8.86	9.64
20	Calculated (as $C_{19}H_{21}O_3SCl$ )	62.53	5.81	8.79	9.71

## Example 3

Synthesis of 2-bromo-1-(4-chlorophenyl)-4,4-dimethyl-1-phenylsulfonylpentan-3-one:-

1-(4-Chlorophenyl)-4,4-dimethyl-1-phenylsulfonylpentan-3-one (5.0 g) was dissolved in a mixture  
 25 of 100 ml of chloroform and 100 ml of acetic acid. To

- 1 this solution, 2.2 g of bromine was added dropwise at 50°C. The mixture was kept at 50°C for 3 hours and then washed with ice-water and an aqueous solution of sodium bicarbonate. The chloroform layer was evaporated and
- 5 the solid residue was crystallized in a mixture of carbon tetrachloride and n-hexane. The crystals were collected by filtration and dried to give 5.8 g of the captioned compound. m.p. 167-168°C.

## Elementary analysis

	C(%)	H(%)	S(%)	Cl(%)	Br(%)
Found	51.55	4.48	7.20	8.05	17.90
Calculated (as $C_{19}H_{20}O_3SClBr$ )	51.42	4.55	7.22	7.99	18.00

## Example 4

- 10 Synthesis of 1-(4-chlorophenyl)-4,4-dimethyl-1,2-bis(1,2,4-triazol-1-yl)pentan-3-one:-

A mixture of 1.1 g of potassium carbonate, 0.56 g of triazole and 30 ml of acetonitrile was refluxed for 1 hour, and a solution of 1.8 g of 2-bromo-1-(4-chlorophenyl)-4,4-dimethyl-1-phenylsulfonylpentan-3-one

15 in 30 ml of acetonitrile was added thereto. The mixture was refluxed for 2 hours. After the removal of the undissolved by filtration, the mixture was concentrated. Ice water was added to the residue and extracted with

20 chloroform. The chloroform layer was evaporated to give 1.5 g of oily substance, which was then dissolved in chloroform and crystallized by adding n-hexane. The

1 crystals were collected by filtration and dried to  
give 1.38 g of the captioned compound (96%). m.p.  
157 - 161°C.

Elementary analysis	C(%)	H(%)	N(%)	Cl(%)
Found	57.02	5.38	23.35	9.73
Calculated (as $C_{17}H_{19}N_6OCl$ )				
	56.89	5.35	23.42	9.88

Example 5

5 Synthesis of 1-(4-chlorophenyl)-4,4-dimethyl-1-phenylsulfonyl-1-penten-3-one:-

2-Bromo-1-(4-chlorophenyl)-4,4-dimethyl-1-phenylsulfonylpentan-3-one (4.44 g) and triazole (2.76 g) were dissolved in dimethylformamide (30 ml), and the  
10 solution was refluxed for 2 hours. After cooling, it was poured into 100 ml of water and extracted with 100 ml of chloroform. The chloroform layer was washed for three times with water, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The  
15 residue was crystallized in n-hexane, and the crystals were collected by filtration and dried to give 2.65 g of 1-(4-chlorophenyl)-4,4-dimethyl-1-phenylsulfonyl-1-penten-3-one. m.p. 135 - 136°C.

Elementary analysis	C(%)	H(%)	S(%)	Cl(%)
Found	62.91	5.35	8.71	9.65
Calculated (as $C_{19}H_{19}O_3SCl$ )				
	62.88	5.29	8.83	9.77

1           It seems that triazole acts as a hydrobromic  
acid - capture in this reaction. On the TLC of the mother  
liquid of the crystallization of the product, a slight  
spot with the Rf value corresponding to that of the  
5 triazole-substituted compound was observed, but the com-  
pound could not be isolated. It is considered that in the  
absence of a base the addition of triazole to the sulfonyl-  
vinyl ketone compounds proceeds only in a very low yield  
even when it is conducted in excessive amounts of triazole.

10 Example 6

Synthesis of 1-(4-chlorophenyl)-4,4-dimethyl-1,2-  
bis(1,2,4-triazol-1-yl)pentan-3-one:-

A mixture of 1.04 g of triazole, 2.07 g of  
anhydrous potassium carbonate and 30 ml of acetonitrile  
15 was refluxed for 1 hour with stirring. After cooling,  
4.44 g of 1-(4-chlorophenyl)-4,4-dimethyl-1-phenyl-  
sulfonyl-1-penten-3-one was added to the mixture and  
reacted at 25°C for 1 hour and for 5 hours under reflux.  
After the removal of the undissolved by filtration, the  
20 mixture was treated in the same way as that of Example  
4, and 2.52 g of the crude product was obtained.  
The crude product was purified by a column chromatography  
on silica gel to give 2.12 g of the captioned compound.  
m.p. 157 - 161°C.

Elementary analysis	C(%)	H(%)	N(%)	Cl(%)
Found	56.70	5.33	23.50	9.92

- 21 -

Calculated (as  $C_{17}H_{19}N_6OCl$ )

56.89 5.35 23.42 9.88

## 1 Example 7

Synthesis of 1-(4-chlorophenyl)-4,4-dimethyl-2-  
(1,2,4-triazol-1-yl)-1-penten-3-one:-

1-(4-Chlorophenyl)-4,4-dimethyl-1,2-bis(1,2,4-  
 5 triazol-1-yl)-pentan-3-one (0.5 g) was heated at 180°C  
 for 1 hour and at 200°C for 3 hours on an oil bath. After  
 cooling, the mixture was dissolved in chloroform (50 ml),  
 washed with water (50 ml) and concentrated to give yellow  
 oily substance (0.37 g). Triazole (0.095 g; 99%) was  
 10 recovered from the aqueous layer by concentration. The  
 oily substance was analyzed by the gas-chromatography  
 under the following conditions:

Apparatus: Nihon Denki 20K type FID detector

Column: 5%XE-60 Chromosorb W carrier, 1 m glass  
 15 column

Column Temperature: 200°C

Vaporizing Room temperature: 240°C

Carrier gas pressure: 1.0 Kg/cm<sup>2</sup>

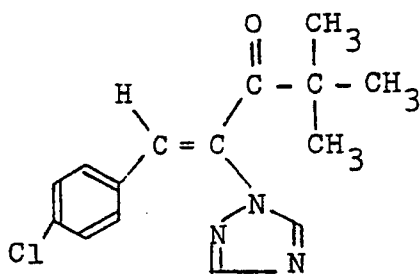
Two peaks were observed at retention times  
 20 300 sec., and 360 sec. (peak area ratio: 36/64).

Elementary analysis of the oily substance

	C(%)	H(%)	N(%)	Cl(%)
Found	62.20	5.45	14.38	12.42
Calculated (as $C_{15}H_{16}N_3OCl$ )	62.17	5.58	14.50	12.23

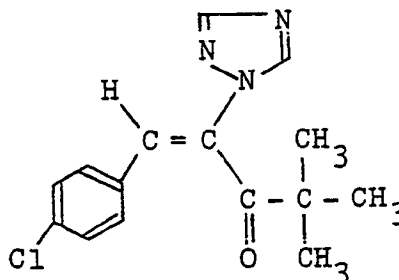
1           This elementary analysis data agrees with that  
 of 1-(4-chlorophenyl)-4,4-dimethyl-2-(1,2,4-triazol-1-yl)-  
 1-penten-3-one. The captioned compound has a double  
 bond and hence is geometrically isomeric. Namely, it  
 5 contains the Z-isomer, wherein the 4-chlorophenyl and  
 triazole are in cis-position, and the E-isomer, wherein  
 the said groups are in trans-position.

The said peaks of the gas-chromatography  
 correspond to those of the E-isomer and Z-isomer, and  
 10 the NMR-spectrum of the substance is the combination  
 of the signals of the both isomers.



Z-Isomer

m.p. 78 - 79°C



E-Isomer

m.p. 108 - 109°C

The elementary analysis and NMR spectrum of  
 each isomer are shown below. The NMR spectrum was  
 measured with deuterio chloroform as solvent, and the  
 15 chemical shift was expressed by  $\delta$  values with tetra-  
 methylsilane as internal standard.

- 23 -

1 E isomer of 1-(4-chlorophenyl)-4,4-dimethyl-  
2-(1,2,4-triazol-1-yl)-1-penten-3-one:

Elementary analysis:

	C(%)	H(%)	N(%)	Cl(%)
Calculated	62.17	5.58	14.50	12.23
(as C <sub>15</sub> H <sub>16</sub> N <sub>3</sub> OCl)				
Found	62.32	5.60	14.41	12.20

NMR spectrum:

8.11 (1H, s, triazole proton)  
7.90 (1H, s, triazole proton)  
7.15 (4H, s, phenyl proton)  
6.99 (1H, s, olefin proton)  
0.99 (9H, s, butyl proton)

Z isomer of 1-(4-chlorophenyl)-4,4-dimethyl-  
2-(1,2,4-triazol-1-yl)-1-penten-3-one (Compound No. 1'):

Elementary analysis:

	C(%)	H(%)	N(%)	Cl(%)
Found	62.35	5.59	14.38	12.18

NMR spectrum:

8.14 (1H, s, triazole proton)  
7.98 (1H, s, triazole proton)  
7.22 (2H, d, phenyl proton, J = 8 Hz)  
6.73 (2H, d, phenyl proton, J = 8 Hz)  
7.49 (1H, s, olefin proton)  
1.22 (9H, s, butyl proton)





- 24 -

## 1 Example 8

Synthesis of 1-(4-chlorophenyl)-4,4-dimethyl-2-  
(1,2,4-triazol-1-yl)-1-penten-3-one:-

A mixture of 0.6 g of 1-(4-chlorophenyl)-  
5 4,4-dimethyl-1,2-bis(1,2,4-triazol-1-yl)-pentan-3-one and  
4 ml of 1,2,4-trichlorobenzene was reacted at 180 - 190°C  
for 4 hours. The reaction mixture was diluted with 50 ml  
of toluene and extracted with 50 ml of 1N hydrochloric  
acid aqueous solution, whereby 1,2,4-triazole was recovered  
10 in the aqueous layer. The organic solvent layer was  
washed with 50 ml of 5% NaHCO<sub>3</sub> aqueous solution, and  
evaporated under reduced pressure to give 0.48 g of the  
captioned compound. The product was found to be a  
mixture of 35 parts of the E-isomer and 65 parts of the  
15 Z-isomer upon the gas-chromatographic analysis. The  
product was subjected to the column chromatography on  
silica gel (50 g) with, as an eluent, a mixture of 1  
part of acetone and 20 parts of n-hexane, thereby 0.15 g  
of the E-isomer and 0.26 g of the Z-isomer were obtained.

## 20 Example 9

Synthesis of 1-(2,4-dichlorophenyl)-4,4-dimethyl-1-  
phenylthiopentan-3-one:-

A mixture of 25.7 g of 2,4-dichlorobenzalpinacolone, Triton-B (4 drops) and 300 ml of ethanol was  
25 heated to 50 - 60°C. Thiophenol (12.1 g) was added  
dropwise to the mixture and refluxed for 6 hours. The  
reaction mixture was concentrated, ice water was added

- 1 thereto, and extracted with ether. After the removal of the ether by distillation, the oily residue was treated with n-hexane, and the resulted crystals were dried to give 30 g of the captioned compound. m.p. 79 - 80°C.

Elementary analysis	C(%)	H(%)	S(%)	Cl(%)
Found	62.02	5.43	8.83	19.41
Calculated	62.12	5.50	8.73	19.30
(as $C_{19}H_{20}OSCl_2$ )				

5 Example 10

Synthesis of 1-(2,4-dichlorophenyl)-4,4-dimethyl-1-phenylsulfonylpentan-3-one:-

- Method A: 1-(2,4-Dichlorophenyl)-4,4-dimethyl-1-phenylthiopentan-3-one (18.3 g) was dissolved in di-  
 10 chloromethane (500 ml), and m-chloroperoxybenzoic acid (19.8 g) was added to the mixture at a temperature of -5°C. The mixture was then treated with the same procedure as that of Example 2 to give 18.3 g of the captioned compound. m.p. 112 - 113°C.

Elementary analysis

	C(%)	H(%)	S(%)	Cl(%)
Found	57.25	4.96	8.01	17.67
Calculated	57.29	4.82	8.05	17.80
(as $C_{19}H_{19}O_3SCl_2$ )				

- 15 Method B: 1-(2,4-Dichlorophenyl)-4,4-dimethyl-1-phenylthiopentan-3-one (9.16 g) was dissolved in acetone (200 ml), and 37% hydrogen peroxide (6.9 g) was added

- 26 -

1 dropwise thereto at 20°C. The mixture was kept at 20°C  
for 12 hours, at 40°C for 1 hour and 60°C for 1 hour.  
After cooling the mixture to 15°C, water (100 ml) was  
gradually added dropwise to it. The resulted precipitates  
5 were collected by filtration and dried to give 9.0 g of  
the captioned compound.

## Example 11

Synthesis of 2-bromo-1-(2,4-dichlorophenyl)-4,4-  
dimethyl-1-phenylsulfonylpentan-3-one:-

10 To a solution of 39.9 g of 1-(2,4-dichloro-  
phenyl)-4,4-dimethyl-1-phenylsulfonylpentan-3-one in  
500 ml of chloroform, 16.8 g of bromine was added drop-  
wise at 60°C and the mixture was then kept at 60°C for  
4 hours. The reaction mixture was treated in the same  
15 way as that of Example 3 to give 44.5 g of crystals  
of the captioned compound. m.p. 135-136°C.

Elementary analysis	C(%)	H(%)	S(%)	Cl(%)	Br(%)
Found	47.82	4.22	6.65	14.71	16.72
Calculated (as C <sub>19</sub> H <sub>19</sub> O <sub>3</sub> SCl <sub>2</sub> Br)	47.71	4.01	6.70	14.83	16.71

## Example 12

Synthesis of 1-(2,4-dichlorophenyl)-4,4-dimethyl-1-  
phenylsulfonyl-1-penten-3-one:-

20 Method A: A solution of 9.6 g of 2-bromo-1-(2,4-di-  
chlorophenyl)-4,4-dimethyl-1-phenylsulfonylpentan-3-one  
and 2.23 g of triethylamine in 100 ml of acetone was

1 refluxed for 3 hours. The mixture was poured into ice  
 water and extracted with 150 ml of ethyl acetate. The  
 organic layer was washed twice with water, dried over  
 anhydrous sodium sulfate, and evaporated under reduced  
 5 pressure. The residue was purified by column chromato-  
 graphy on silica gel using a mixture of n-hexane (20  
 parts) and acetone (1 part) to give 4.8 g of 1-(2,4-  
 dichlorophenyl)-4,4-dimethyl-1-phenylsulfonyl-1-penten-  
 3-one.  $n_D^{25}$  1.5723

Elementary analysis	C(%)	H(%)	S(%)	Cl(%)
Found	57.32	4.46	8.15	17.92
Calculated	57.43	4.58	8.07	17.84
(as $C_{19}H_{18}O_2SCl_2$ )				

10 Method B:

Sodium ethylate was prepared by dissolving 2.3  
 g of metallic sodium in 100 ml of 99% ethanol, which was  
 then mixed with 6.9 g of triazole and stirred for 30  
 minutes. The mixture was evaporated to dryness under  
 15 reduced pressure to give sodium salt of triazole. Thus  
 prepared sodium salt of triazole (0.91 g) was added to  
 a solution of 2-bromo-1-(2,4-dichlorophenyl)-4,4-dimethyl-  
 1-phenylsulfonylpentan-3-one (4.78 g) in acetonitrile  
 (50 ml), and refluxed for 1 hour. After cooling, the  
 20 mixture was added to 200 ml of ice water and extracted  
 with ethyl acetate. The organic layer was then treated  
 in the same manner as that of the method A to give 3.77 g  
 of 1-(2,4-dichlorophenyl)-4,4-dimethyl-1-phenylsulfonyl-

## 1 1-penten-3-one.

## Method C:

To a solution of 4.44 g of 2-bromo-1-(2,4-dichlorophenyl)-4,4-dimethyl-1-phenylsulfonylpentan-3-one in 50 ml of tetrahydrofuran, a solution of 0.56 g of potassium hydroxide in 30 ml of water was added dropwise and vigorously stirred for 3 hours. The reaction mixture was combined with 100 ml of ice water, and extracted with 100 ml of chloroform. The organic solvent layer was washed twice with water, dried over anhydrous sodium sulfate, and evaporated under reduced pressure to give 3.61 g of 1-(2,4-dichlorophenyl)-4,4-dimethyl-1-phenylsulfonyl-1-penten-3-one.

## Example 13

15 Synthesis of 1-(2,4-dichlorophenyl)-4,4-dimethyl-1,2-bis(1,2,4-triazol-1-yl)pentan-3-one:-

A mixture of 3.97 g of 1-(2,4-dichlorophenyl)-4,4-dimethyl-1-phenylsulfonyl-1-penten-3-one, 2.07 g of triazole, 0.69 g of potassium carbonate and 50 ml of acetonitrile was refluxed for 12 hours. After cooling, the mixture was treated in the same manner as that of Example 4 to give 4.2 g of oily substance. This substance was purified by column chromatography on silica gel to give 3.85 g of the captioned compound.  $n_D^{28}$  1.5445.

25	Elementary analysis	C(%)	H(%)	N(%)	Cl(%)
	Found	51.85	4.63	21.43	17.92

Calculated 51.91 4.62 21.37 18.03  
 (as  $C_{17}H_{18}N_6OCl_2$ )

1 Example 14

Synthesis of 1-(2,4-dichlorophenyl)-4,4-dimethyl-1,2-bis(1,2,4-triazol-1-yl)pentan-3-one:-

- A mixture of 1.4 g of triazole, 2.8 g of  
 5 potassium carbonate and 60 ml of acetonitrile was heated  
 under reflux for 2 hours. After cooling, 4.8 g of 2-  
 bromo-1-(2,4-dichlorophenyl)-4,4-dimethyl-1-phenylsulfonyl-  
 pentan-3-one was added to the mixture, which was then  
 reacted at 20°C for 1 hour, and under reflux for 2 hours.  
 10 The reaction mixture was treated in the same way as that  
 of Example 4 to give 3.5 g of oily substance, which was  
 purified by column chromatography on silica gel to give  
 3.12 g of 1-(2,4-dichlorophenyl)-4,4-dimethyl-1,2-bis(1,2,4-  
 triazol-1-yl)pentan-3-one as oil.  $n_D^{27}$  1.5440

Elementary analysis	C(%)	H(%)	N(%)	Cl(%)
Found	51.87	4.71	21.36	17.89
Calculated				
(as $C_{17}H_{18}N_6OCl_2$ )	51.91	4.62	21.37	18.03

- 15 Thus obtained product contains two diastereomer,  
 and may further be isolated by column chromatography on  
 silica gel. This product can be used for the next step,  
 the heat-decomposition without any further isolation.

## 1 Example 15

Synthesis of 1-(2,4-dichlorophenyl)-4,4-dimethyl-2-  
(1,2,4-triazol-1-yl)-1-penten-3-one:-

1-(2,4-Dichlorophenyl)-4,4-dimethyl-1,2-bis(1,2,4-  
5 triazol-1-yl)pentan-3-one (1.0 g) was heated under the  
same conditions as those of Example 7 and the 0.73 g of  
pale yellow oily substance was obtained by treating the  
reaction mixture in the same way as that of Example 7.  
Triazole 0.172 g was recovered from the aqueous layer.  
10 This oily substance was analyzed by gas chromatography  
under the same conditions as Example 7, and two peaks  
(peak area 37/63) due to the E- and Z-isomers were  
observed.

Elementary analysis data of the substance:

	C(%)	H(%)	N(%)	Cl(%)
Found	55.41	4.55	13.10	21.72
Calculated				
(as C <sub>15</sub> H <sub>14</sub> N <sub>3</sub> OC <sub>12</sub> )	55.56	4.67	12.96	21.87

The NMR spectrum of the substance is the combi-  
15 nation of the signals of the E- and Z-isomers.

The E- and Z-isomers of 1-(2,4-dichlorophenyl)-  
4,4-dimethyl-2-(1,2,4-triazol-1-yl)-1-penten-3-one have  
the following NMR spectrums.

Isomer	NMR Spectrum
E-Isomer m.p. 92 - 93°C	8.30 (1H, s, triazole-proton) 8.04 (1H, s, triazole-proton) 7.26 (2H, m, phenyl-proton) 7.45 (1H, m, phenyl 3-position proton) 7.22 (1H, s, olefin-proton) 0.97 (9H, s, butyl-proton)
Z-Isomer m.p. 119 - 120°C	7.94 (1H, s, triazole-proton) 7.80 (1H, s, triazole-proton) 7.46 (1H, s, olefin-proton) 7.33 (1H, d, phenyl 3-position proton, J=3 Hz) 6.95 (1H, d, phenyl 5-position proton, J=3 Hz, 8 Hz) 6.40 (1H, d, phenyl 6-position proton, J=8 Hz) 1.27 (9H, s, butyl-proton)

## 1 Example 16

Synthesis of 1-(2,4-dichlorophenyl)-1-p-toluene-  
sulfonyl-4,4-dimethylpentan-3-one:-

Step 1: Synthesis of 1-(2,4-dichlorophenyl)-1-p-  
5 methylphenylthio-4,4-dimethylpentan-3-one:

A mixture of 50 g of 2,4-dichlorobenzalpine-  
colone, 25 g of p-methylphenylthiol, 0.5 g of Triton-B  
and 400 ml of ethanol was heated under reflux for 4 hours.  
After the removal of the solvent by distillation under  
10 reduced pressure, 300 ml of ice water was added to the



1 residue and extracted with ether. The ether layer was  
washed with 5% potassium carbonate aqueous solution and  
evaporated. The residue was added to 100 ml of n-hexane  
to give 70 g of crystalline 1-(2,4-dichlorophenyl)-1-  
5 p-methylphenylthio-4,4-dimethylpentan-3-one. m.p. 65 -  
66°C.

Step 2: Synthesis of 1-(2,4-dichlorophenyl)-1-p-  
toluenesulfonyl-4,4-dimethylpentan-3-one:

To a solution of 20 g of 1-(2,4-dichlorophenyl)-1-  
10 p-methylphenylthio-4,4-dimethylpentan-3-one in 500 ml  
of dichloromethane, 20 g of m-chloroperoxybenzoic acid  
was added at -5°C, and the mixture was stirred at a  
room temperature for 3 hours. The reaction mixture  
was washed with 5% sodium hydrogensulfite aqueous  
15 solution and with sodium bicarbonate aqueous solution,  
and evaporated to give 21 g of the captioned compound.  
 $n_D^{27}$  1.5563.

#### Example 17

In the same manner as in Example 16, but using  
20 p-chlorophenylthiol instead of p-methylphenylthiol, 1-  
(2,4-dichlorophenyl)-1-(4-chlorophenylthio)-4,4-dimethyl-  
pentan-3-one, m.p. 122 - 123°C and 1-(2,4-dichlorophenyl)-  
1-(4-chlorophenylsulfonyl)-4,4-dimethylpentan-3-one,  
m.p. 184 - 185°C were obtained.

## 1 Example 18

Synthesis of 1-(4-chlorophenyl)-4,4-dimethyl-1-p-toluenesulfonylpentan-3-one:-

A mixture of 3 g of 4-chlorobenzalpinacolone,  
5 2 g of p-toluenesulfinic acid and 15 ml of ethanol was refluxed for 8 hours and then allowed to stand at a room temperature overnight. The collection of the precipitated crystals gave 4.8 g of the captioned compound (yield: 94%). m.p. 170 - 171°C.

## 10 Example 19

Synthesis of 1-(2,4-dichlorophenyl)-4,4-dimethyl-1-p-toluenesulfonylpentan-3-one:-

A mixture of 10 g of 2,4-dichlorobenzalpinacolone, 7.3 g of p-toluenesulfinic acid, 4.1 g of  $\text{NaH}_2\text{PO}_3$   
15 and 70 ml of 90% aqueous alcohol was heated under reflux for 8 hours. After cooling, 400 ml of ice water was added to the reaction mixture and extracted with 500 ml of ethyl acetate. The organic solvent layer was washed with 400 ml of 5% sodium bicarbonate aqueous solution and  
20 400 ml of ice water and evaporated under reduced pressure to give 16 g of the captioned compound (yield 99%).  
 $n_D^{27}$  1.5563.

## Example 20

The bromination of 1-(2,4-dichlorophenyl)-1-p-  
25 toluenesulfonyl-4,4-dimethylpentan-3-one was carried out in the same manner as that of Example 3 but using 25 g

- 34 -

1 of 1-(2,4-dichlorophenyl)-1-p-toluenesulfonyl-4,4-  
dimethyl-3-one, 9.2 g of bromine, 200 ml of acetic acid  
and 300 ml of chloroform, and 29 g of 2-bromo-1-(2,4-  
dichlorophenyl)-4,4-dimethyl-1-p-toluenesulfonylpentan-3-  
5 one was obtained.

## Example 21

The bromination of 1-(2,4-dichlorophenyl)-  
4,4-dimethyl-1-(4-chlorophenylsulfonyl)-pentan-3-one  
was carried out in the same manner as that of Example 3  
10 but using 25 g of 1-(2,4-dichlorophenyl)-1-(4-chloro-  
phenylsulfonyl)-4,4-dimethylpentan-3-one, 8.9 g of  
bromine, 200 ml of acetic acid and 300 ml of chloroform,  
and 24.4 g of 2-bromo-1-(2,4-dichlorophenyl)-4,4-  
dimethyl-1-(4-chlorophenylsulfonyl)pentan-3-one was  
15 obtained. m.p. 184 - 185°C.

## Example 22

Synthesis of 1-(2,4-dichlorophenyl)-4,4-dimethyl-1-  
p-toluenesulfonyl-1-penten-3-one:-

## Method A:

20 To a solution of 1 g of 2-bromo-1-(2,4-di-  
chlorophenyl)-4,4-dimethyl-1-p-toluenesulfonylpentan-3-  
one in 30 ml of tetrahydrofuran, a solution of 0.12 g  
of potassium hydroxide in 10 ml of water was added  
dropwise under ice-cooling. The mixture was stirred  
25 under ice-cooling for 3 hours. After adding 100 ml of  
water, the mixture was extracted with 100 ml of chloroform.

1 The chloroform layer was evaporated under reduced  
pressure, and the residue was crystallized with n-hexane  
to give 0.5 g of the captioned compound. m.p. 104 -  
105°C.

5 Method B:

To a solution of 4.9 g of 2-bromo-1-(2,4-  
dichlorophenyl)-4,4-dimethyl-1-p-toluenesulfonylpentan-  
3-one in a mixture of 150 ml of acetonitrile and 150 ml  
of tetrahydrofuran, 1.0 g of sodium salt of triazole  
10 was added. The mixture was stirred under ice-cooling  
for 5 hours. After the addition of 500 ml of water,  
the mixture was extracted with 500 ml of chloroform.  
The chloroform layer was evaporated, and the residue  
was crystallized with n-hexane to give 4 g of the captioned  
15 compound. m.p. 104 - 105°C.

Example 23

Synthesis of 1-(2,4-dichlorophenyl)-4,4-dimethyl-  
1,2-bis(1,2,4-triazol-1-yl)pentan-3-one:-

Method A:

20 With the same procedures as those of Example 4  
but using 5 g of 2-bromo-1-(2,4-dichlorophenyl)-4,4-  
dimethyl-1-p-toluenesulfonylpentan-3-one, 1.4 g of  
triazole, 2.8 g of potassium carbonate, and 60 ml of  
acetone, 3.2 g of the captioned compound was obtained as  
25 oily substance.  $n_D^{27}$  1.5440.

- 36 -

## 1 Method B:

With the same procedures as those of Example 4  
but using 5 g of 2-bromo-1-(2,4-dichlorophenyl)-4,4-  
dimethyl-1-(4-chlorophenylsulfonyl)pentan-3-one, 1.4 g  
5 of triazole, 2.8 g of potassium bicarbonate and 60 ml  
of acetonitrile, 2.9 g of the captioned compound as oily  
substance was obtained.

## Method C:

With the same procedures as those of Example 13  
10 but using 2 g of 1-(2,4-dichlorophenyl)-4,4-dimethyl-1-  
p-toluenesulfonyl-1-penten-3-one, 1 g of triazole, 0.35 g  
of potassium carbonate and 50 ml of acetonitrile, 1.8 g  
of the captioned compound was obtained.

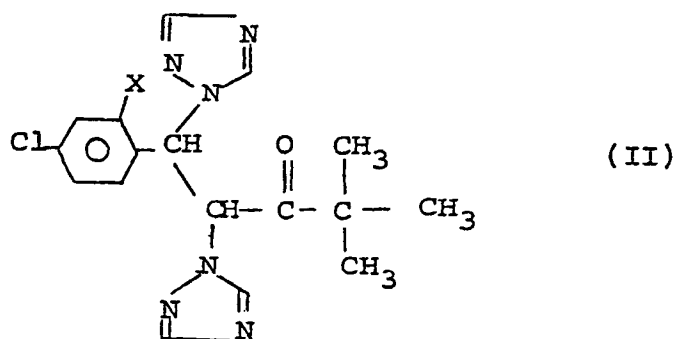
- 1 The present compounds (II) - (VI) obtained by above methods are shown in Table 1.

Table 1

Compound of the formula	X	Y	Physical constant
(II)	H Cl	- -	mp 157 - 161°C $n_D^{28}$ 1.5445
(III)	H H Cl Cl Cl	H CH <sub>3</sub> Cl H CH <sub>3</sub>	mp 135 - 136°C mp 91 - 92°C mp 97 - 98°C $n_D^{25}$ 1.5723 mp 104 - 105°C
(IV)	H H Cl Cl Cl	H CH <sub>3</sub> Cl H CH <sub>3</sub>	mp 167 - 168°C mp 167 - 168°C mp 184 - 185°C mp 135 - 136°C mp 175 - 176°C
(V)	H H Cl Cl Cl	H CH <sub>3</sub> Cl H CH <sub>3</sub>	mp 145 - 146°C mp 170 - 171°C mp 184 - 185°C mp 112 - 113°C $n_D^{27}$ 1.5563
(VI)	H Cl Cl Cl	H CH <sub>3</sub> Cl H	mp 127 - 128°C mp 65 - 66°C mp 122 - 123°C mp 79 - 80°C

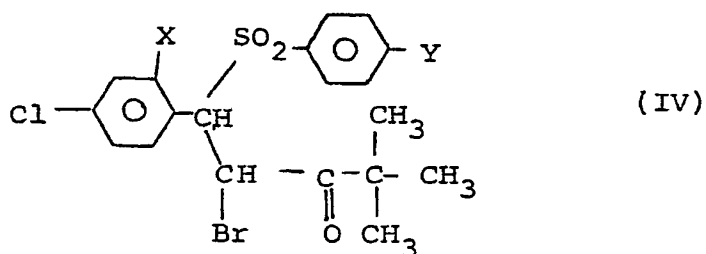
## C L A I M S

1. A compound of the formula:



wherein X is a hydrogen or chlorine atom.

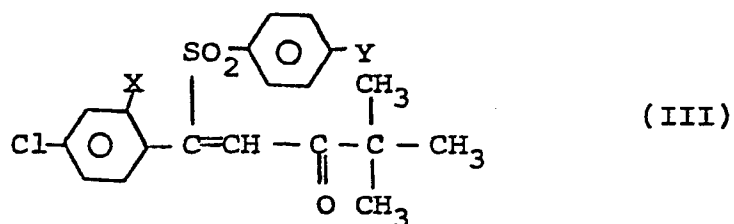
2. A process of producing a compound of the formula (II) as claimed in claim 1, which comprises reacting a compound of the formula:



wherein X is as defined in claim 1 and Y is a hydrogen or chlorine atom or a methyl group, with triazole.

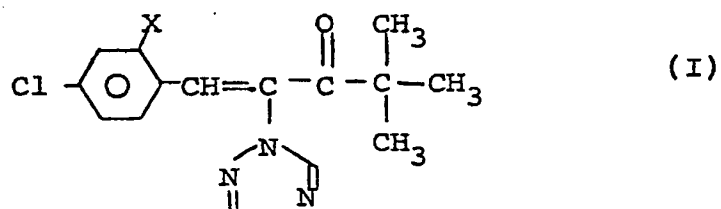
3. A process of producing a compound of the formula (II) as claimed in claim 1, which comprises reacting a compound of the formula:

- 39 -

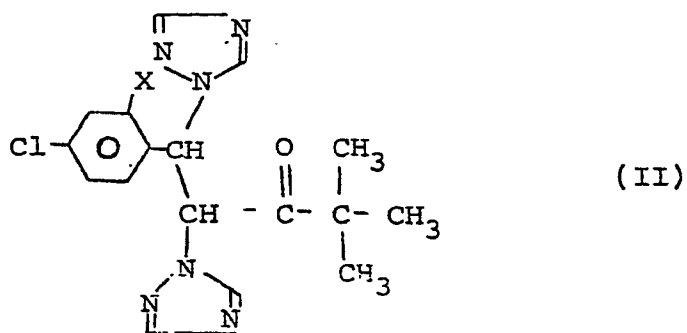


wherein X is as defined in claim 1 and Y is a hydrogen or chlorine atom or a methyl group, with triazole.

4. A process of producing a compound of the formula:



wherein X is as defined in claim 1, which comprises heating a compound of the formula:



wherein X is as defined in claim 1.

5. A process according to claim 4, wherein the heating is carried out at 50° to 200°C.



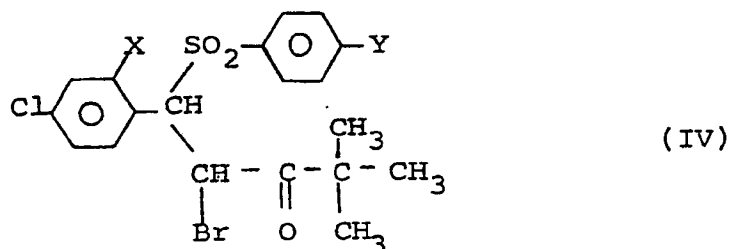
- 40 -

6. A process according to claim 4 or 5 wherein the heating is carried out in the presence of a solvent which is a ketone, halogenated hydrocarbon, aromatic hydrocarbon, nitrile, ether, dimethylformamide, dimethylsulfoxide, hexamethylphosphoramide or water.

7. A process according to any one of claims 4 to 6 wherein the compound of the formula (II) is prepared by a process as claimed in claim 2.

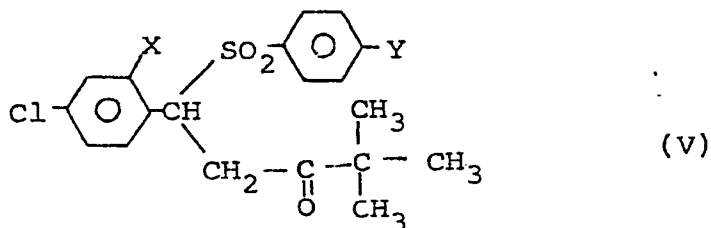
8. A process according to any one of claims 4 to 6 wherein the compound of the formula (II) is prepared by a process as claimed in claim 3.

9. A process according to claim 3 or 8 wherein the compound of the formula (III) is prepared by reacting a compound of the formula:



wherein X and Y are as defined in claim 3, with a base.

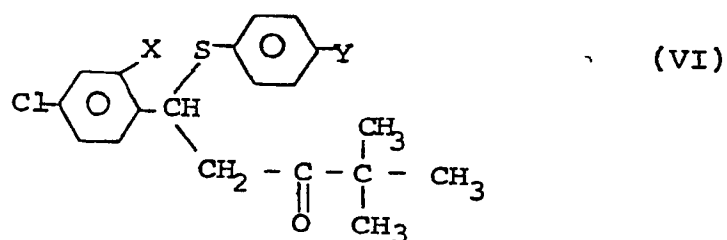
10. A process according to claim 2, 7 or 9, wherein the compound of the formula (IV) is prepared by reacting a compound of the formula:



- 41 -

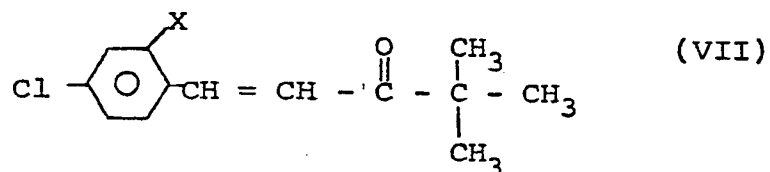
wherein X and Y are as defined in claim 2, with a brominating agent.

11. A process according to claim 10 wherein the compound of the formula (V) is prepared by reacting a compound of the formula:

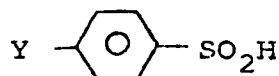


wherein X and Y are as defined in claim 10, with an oxidizing agent.

12. A process according to claim 10, wherein the compound of the formula (V) is prepared by reacting a compound of the formula:



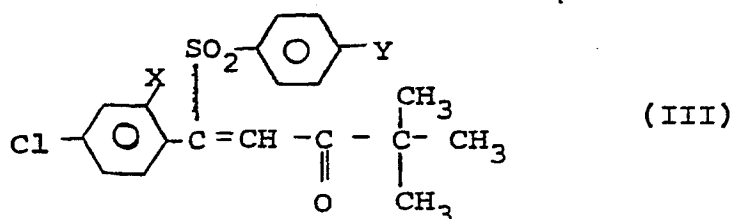
wherein X is as defined in claim 10, with a compound of the formula:



- 42 -

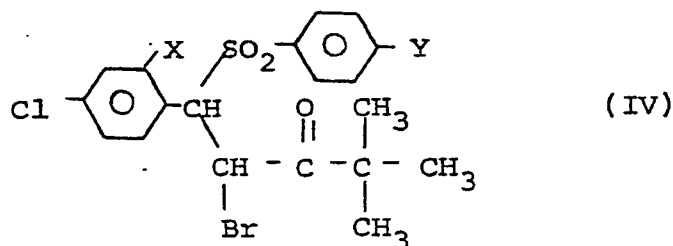
wherein Y is as defined in claim 10.

13. A compound of the formula:



wherein X is a hydrogen or chlorine atom, and Y is a hydrogen or chlorine atom or a methyl group.

14. A process of producing a compound of the formula (III) as claimed in claim 13, which comprises reacting a compound of the formula:



wherein X and Y are as defined in claim 13, with a base.

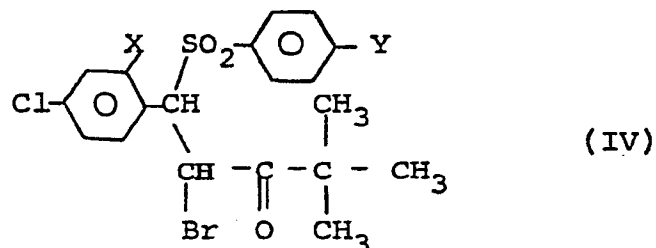
15. A process according to claim 2, 3, 7, 8, 9 or 14 wherein the reaction is carried out with a base which is a carbonate, acetate, hydroxide of a metal or tertiary amine.

16. A process according to claim 2, 3, 7, 8, 9, 14 or 15, wherein the reaction is carried out in a solvent which is a ketone, nitrile, aromatic hydrocarbon, ether, dimethylformamide,

- 43 -

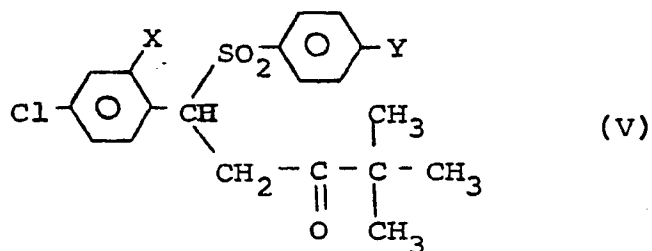
dimethylsulfoxide, hexamethylphosphoramide, water or a mixture thereof, at 0°C to the boiling point of the solvent employed.

17. A compound of the formula:



wherein X is a hydrogen or chlorine atom, and Y is a hydrogen or chlorine atom or a methyl group.

18. A process of producing a compound of the formula (IV) as claimed in claim 17, which comprises reacting a compound of the formula:



wherein X and Y are as defined in claim 17, with a brominating agent.

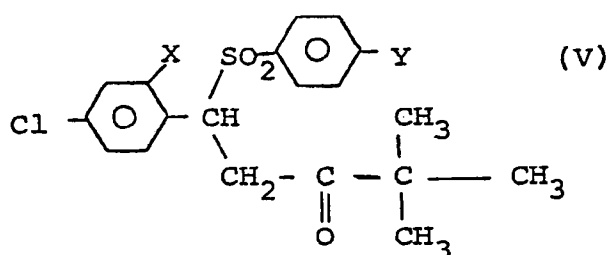
19. A process according to claim 10 or 18 wherein the brominating agent is bromine or N-bromosuccinimide.

20. A process according to claim 10, 18 or 19, wherein the reaction is carried out in

- 44 -

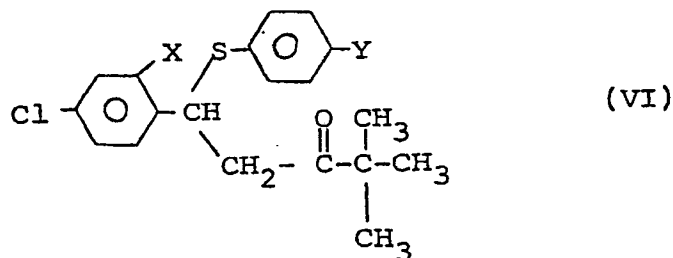
a solvent which is a halogenated hydrocarbon, halogenated aromatic hydrocarbon, ether, water, methanol, pyridine, dimethylformamide or acetic acid, at 0°C to the boiling point of the solvent employed.

21. A compound of the formula:



wherein X is a hydrogen or chlorine atom, and Y is a hydrogen or chlorine atom or a methyl group.

22. A process of producing a compound of the formula (V) as claimed in claim 21, which comprises reacting a compound of the formula:



wherein X and Y are as defined in claim 21, with an oxidizing agent.

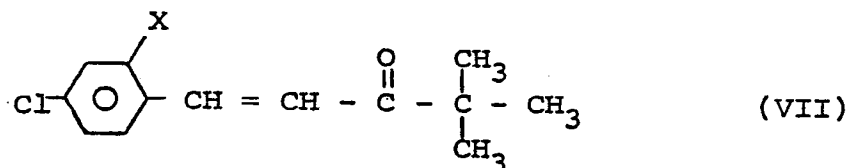
23. A process according to claim 11 or 22 wherein the oxidizing agent is hydrogen peroxide, an organic acid peroxide, potassium

- 45 -

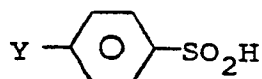
permanganate, sodium metaperiodate, nitric acid, sodium hypochlorite, ozone or chromic acid.

24. A process according to claim 11, 22 or 23 wherein the reaction is carried out in a solvent which is a halogenated hydrocarbon, ketone, acetic acid or water, at  $-50^{\circ}$  to  $100^{\circ}\text{C}$ .

25. A process of producing a compound of the formula (V) as claimed in claim 21, which comprises reacting a compound of the formula:



wherein X is as defined in claim 21, with a compound of the formula:



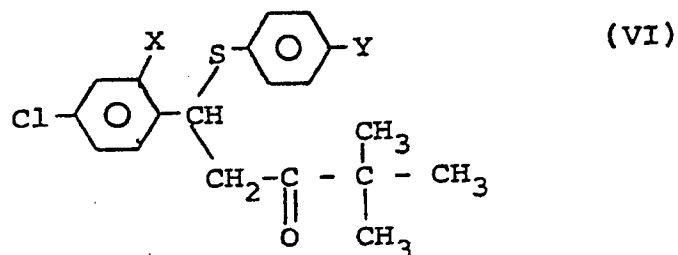
wherein Y is as defined in claim 21.

26. A process according to claim 12 or 25 wherein the reaction is carried out in a solvent which is an alcohol, hydrocarbon, ketone, nitrile, ether, dimethylformamide, dimethylsulfoxide, water or a mixture thereof, at  $0^{\circ}\text{C}$  to the boiling point of the solvent employed.

27. A process according to claim 12, 25 or 26, wherein the reaction is carried out in the presence of a base which is pyridine, Triton B or sodium phosphite.

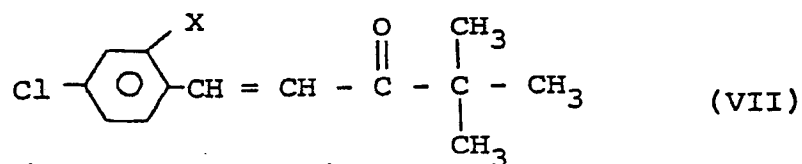
- 46 -

28. A compound of the formula:

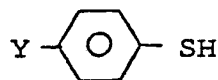


wherein X is a hydrogen or chlorine atom, and Y is a hydrogen or chlorine atom or a methyl group.

29. A process of producing a compound of the formula VI as claimed in claim 28 which comprises reacting a compound of the formula:



wherein X is as defined in claim 28, with a compound of the formula:



wherein Y is as defined in claim 28.

30. A process according to claim 29, wherein the reaction is carried out in a solvent

- 47 -

which is an alcohol, aromatic hydrocarbon, ketone, nitrile, ether, dimethylformamide, dimethylsulfoxide or an aqueous mixture thereof, at 0°C to the boiling point of the solvent employed.